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Investigation of as-grown nitrogen-doped Czochralski silicon

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ABSTRACT

Two Czochralski (CZ) silicon ingots, named NCZ and ACZ silicon, were grown under the same procedure in nitrogen and an argon atmosphere respectively. The experiments reveal that nitrogen was doped into the silicon ingot and N-O complexes were generated during the crystal growth, while it was grown in a nitrogen atmosphere. The nitrogen concentration profile in the NCZ silicon ingot indicates that the nitrogen concentration in the wafer edges was less than that in the center. It is also found that the as-grown oxygen-thermal donors were almost same. Furthermore, it is discovered that the profile of phosphorus concentration in NCZ silicon was also the same as that in ACZ silicon. It is considered that compared with argon atmosphere, nitrogen atmosphere has no influence on the evaporation rates of phosphorus from melting silicon.

Keywords: nitrogen doping, oxygen, silicon.

1. INTRODUCTION

In recent years, nitrogen behavior in single crystal silicon has been intensively studied. In general, nitrogen is used as a protective gas or a carrier gas in manufacture processes of very large scale integration (VLSI). It is well known that nitrogen atoms exist in silicon as pairs.¹ It has been found that nitrogen in silicon can suppress microdefects, and lock dislocations to increase mechanical strength.^{2,3} Due to the contamination of quartz crucible Oxygen is main impurity in CZ silicon. It has been widely reported that thermal donors(TDs), which affect the electrical stability of silicon material and devices, are produced in CZ silicon annealed in the temperature range 300-550°C.⁴ It was also reported that nitrogen in CZ silicon can slightly suppress the generation of thermal donors⁵, and interact with oxygen atoms to form nitrogen-oxygen (N-O) complexes which are a kind of donors. However, few papers about the properties of nitrogen in as-grown silicon has been published^{6,7}.

In our experiment, we introduced nitrogen into silicon by growing silicon ingot in a nitrogen ambience. Compared with ACZ, the influences of nitrogen ambience on the introduction of nitrogen, the generation of as-grown thermal donors and Phosphorus evaporation rates from melting silicon has been investigated. It was found the nitrogen was induced into silicon ingot and the N-O complexes were generated during crystal growth. It is considered that nitrogen atmosphere has no influence on the thermal donors, the evaporation rates of phosphorus and the concentration profile phosphorus in silicon ingot.

2. EXPERIMENT

The n-type <111> NCZ and ACZ silicon ingots were grown under the same procedure in nitrogen and an argon atmosphere, respectively. And the same amount of phosphor dopant was used. Samples were cut from different sections at the same positions for the two ingots. All samples were 2.0mm in thickness. From head to tail, the ACZ samples are numbered as A0-A3 and the NCZ samples N0-N3.

The samples were checked by a Fourier transform infrared spectrometer (FTIR) at room temperature. A high pure float zone silicon in which the concentration of oxygen, nitrogen and carbon is less than the detection limit of FTIR. The absorption lines at 1107 cm⁻¹ and 963 cm⁻¹ were used to determine the concentration of oxygen and nitrogen, respectively.

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The calibration factor for oxygen is $3.14 \times 10^{17} \text{ cm}^{-2}$ and $1.82 \times 10^{17} \text{ cm}^{-2}$ for nitrogen. Furthermore, the samples were annealed at 650°C for 30 min. and 900°C for 2 h to eliminate as-grown TDs and N-O complexes, respectively. Before and after annealing, the resistivity of the samples was measured. A four-point probe technique was used to measure the resistivity of samples. The resistivity was then converted into the carrier concentration according to the ASTM F723-88 standard.

3. RESULTS AND DISCUSSION

3.1. Nitrogen and N-O complex in as-grown nitrogen doped silicon

Nitrogen pairs were found in the tail end of NCZ silicon ingot. Fig. 1 shows the FTIR spectrum of NCZ silicon sample from the tail position. It can be seen that the local vibration mode (LVM) absorption line of nitrogen pairs at 963 cm^{-1} was observed. This indicates that nitrogen impurity was introduced into the NCZ silicon ingot. In the NCZ samples from the head position, no relative line at 963 cm^{-1} was detected. It is clear that nitrogen was mainly induced into the tail position, but not the head position. Because the segregation coefficient of nitrogen in silicon is very low (about 1×10^{-4}), it is easily understood that nitrogen concentration in the tail position is higher than that in the head position.

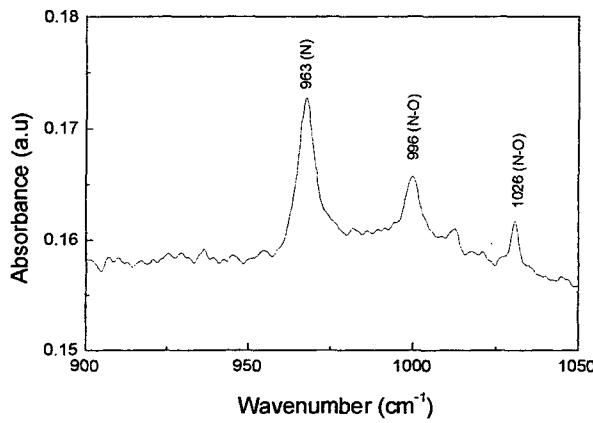


Fig. 1. FTIR spectrum of NCZ silicon sample from the tail position.

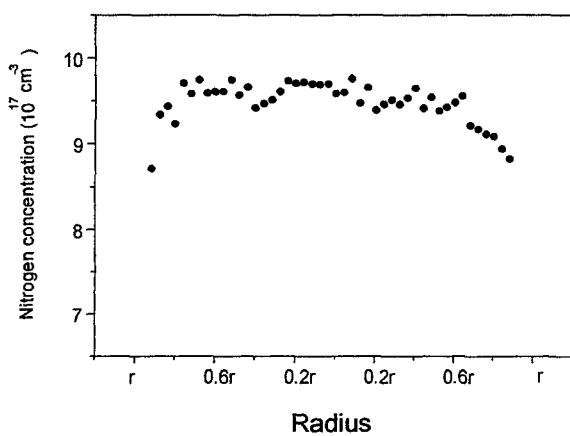


Fig. 2. Nitrogen concentration profile along with the radius of NCZ silicon sample from the tail position.

Meanwhile, the lines at 996 and 1026 cm^{-1} , which were recognized to be LVM of N-O complexes⁷, were observed in Fig. 1. This illustrates that N-O complexes were generated in the tail position of the NCZ silicon ingot during the crystal growth. Again, no LVM lines of N-O complexes in the head position were detected. During cooling processes of crystal, silicon ingots were kept at high temperatures in the furnaces. This means that silicon ingots suffered from heat treatments at different high temperatures. It is considered that during cooling process, nitrogen with higher concentration in the tail position can interact with oxygen to produce the N-O complexes, which existed in as-grown silicon.

Fig. 2 shows the radius profile of nitrogen concentration in the NCZ silicon sample from the tail position. The nitrogen concentration in the edges was less than that in the center. This profile was depended on the condition of crystal growth.

3.2. Effect of nitrogen atmosphere on TDs concentration in as-grown silicon

The samples of NCZ and ACZ silicon were annealed at 650°C for 30 minutes. It is well known that such a heat treatment has been applied to eliminate TDs. After annealing, as-grown TDs in the NCZ and ACZ silicon were annihilated, but the concentration of N-O complex donors in NCZ silicon changed very small.⁸ So we can deduce that the variations of carrier concentration before and after annealing is just owing to the as-grown TDs being annihilated in the annealing process. The as-grown TDs in the NCZ and ACZ silicon is shown in Fig. 3.

It is obvious that the as-grown TDs concentration in the NCZ silicon was the same as that in the ACZ silicon. It was reported that TDs in NCZ silicon annealed at 450°C for 1 h were suppressed⁵. In this experiments, the NCZ silicon ingot was suffered from different annealing in the temperature range of 350 – 550°C . Moreover, the as-grown TDs concentration was up to $1 \times 10^{15} \text{ cm}^{-3}$, which was very higher the possible concentration of N-O complexes. The TDs concentration is

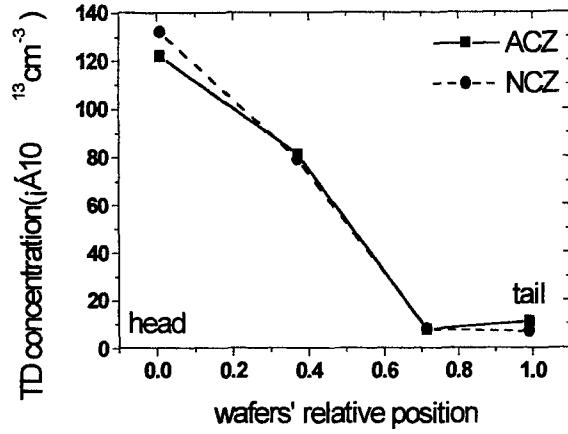


Fig.3. TDs concentration in as-grown silicon.

determined by oxygen concentration and thermal history, which is associated with the sample positions in silicon ingot, but not nitrogen. It was found in the experiments that the oxygen concentration in the different positions of NCZ silicon ingot was similar to that of ACZ silicon ingot. Thus, the concentration of as-grown TDs in both the ingots was almost same (Fig. 3)

3.3. Effect of nitrogen atmosphere on the rates in which P and SiO evaporate from melting silicon

After NCZ and CZ silicon samples were annealed at 900°C for 2 hours, as-grown thermal donors and N-O complexes (only

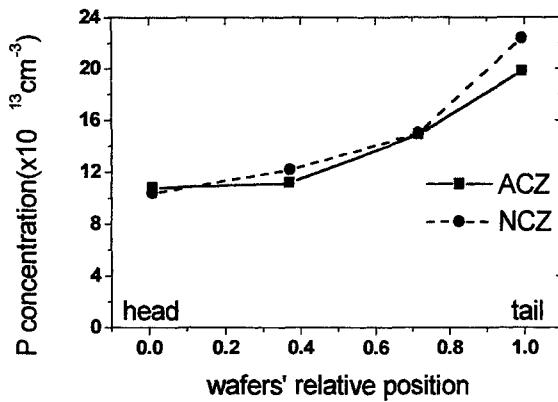


Fig.4. Phosphor concentration in ACZ and NCZ silicon.

in NCZ silicon) were totally annihilated ⁸. And then the carriers in silicon came exactly from the dopant--phosphorus. Fig 4. shows the phosphorous concentration in ACZ and NCZ silicon ingots. We can find the concentration profiles of phosphorus are very similar between ACZ and NCZ silicon. That means that compared with argon atmosphere, pulling crystal in a nitrogen atmosphere has no influences on the evaporation rates of phosphorus from melting silicon.

4. CONCLUSIONS

Two CZ silicon ingots were grown in nitrogen and an argon atmosphere, respectively. It is found that in comparison with argon atmosphere, nitrogen was introduced into NCZ silicon ingot, and N-O complexes were formed during the crystal

growth. Nitrogen atmosphere has no influence on TDs concentration in as-grown silicon and the evaporation rates of phosphorus from melting silicon.

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